MPA MaterialsMatter

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INSIDE

Gang Wu

Getting a charge out of exploring new avenues to clean, renewable energy

By Francisco Ojeda
ADEPS Communications

For the first time Gang Wu is taking on the challenge of leading a project at Los Alamos National Laboratory—and he's looking forward to the tests presented.

"I am really excited to take the next step in my career," said Wu, principal investigator of a venture using a novel approach to designing and synthesizing an efficient air cathode for use in lithium-air batteries. "This is a leadership opportunity. It gives me a chance to manage a project from start to finish rather than just doing one part. Now I see the whole thing through."

Lithium-air batteries have the potential to power a family car for 500 miles on a single charge—a distance up to 10 times greater than provided by traditional lithium-ion batteries in electric vehicles. The air cathode in the lithium-air battery appears to offer this promise, because it takes oxygen from atmosphere, and, if focused correctly, can catalyze the unlimited cathode reactant, greatly increasing the electricity that usually batteries can store. However, to realize the potential of these devices critical scientific challenges must be overcome, especially the development of efficient and cost-effective cathode catalyst.

In addition to setting the experiment's goals and managing their completion, Wu, a member of Sensors and Electrochemical Devices (MPA-11), performs the catalyst synthesis and testing. The project includes Wu's mentor Piotr Zelenay (MPA-11), who oversees electrochemistry testing, and Yusheng Zhao of the Lujan Neutron Scattering Center, who conduct complementary neutron scattering to study the behavior of lithium-ions in air cathodes during the charging and discharging process.

Wu and his collaborators in the Laboratory Directed Research and Development Early Career Research Program project envision the creation of a sustainable, high-energy-density, low-cost electrochemical storage device. The work supports the Laboratory's energy security mission.

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From David's Desk

MPA Division finished fiscal year 2010 (FY10) having spent $73.4 million (M). Our allocation at year-end was $94.6M, reflecting the fact that much of our funding carries over from year to year. I thought I would use this "From the desk" article to provide a little perspective on where we are financially.

First, it is useful to look at costs. In FY09 and FY10, MPA spent $61.0M and $70.6M, respectively—the increase resulting from a combination of increased number of personnel and a significant increase in labor rates. The continuing increase in FY11 is more along the lines of the increases we might expect from inflation, with some impact from an increase in the number of personnel. The year-end allocation for MPA is always higher than the spending, because a fair fraction of our funds must carry over from one year to the next. Looking at funds allocated within a given fiscal year gives a better picture. So, for FY09, 10, and 11 respectively, MPA got $65.4M, $77.3M, and $63.8M in newly allocated funding.

To be fair, some of the funds we got in FY10 came late and were intended for FY11. We have $21.2M in carryover for FY12, and many of our programs are healthy. We don't need to carry over quite so much into FY13, but we also benefit from having a cushion above the amount we need simply to meet programmatic expectations. Our challenge in FY12 is to generate enough over $70M in new allocations that we continue to have a healthy budget, with a good amount of carryover, when our average new funding has been more like $69M.

"I thought I would use this 'From the desk' article to provide a little perspective on where we are."

While this is a challenge, MPA continues to be very competitive in responding to proposal solicitations. We have been successful enough in LDRD that our funding in FY12 will be up from FY11. The DOE Office of Science funding looks solid for FY12, and we have several employees pursuing opportunities for new BES funding. The applied energy programs picture is mixed, and it may be somewhat premature to try to estimate how this will go. We have known for some time that the DOE Office of Electricity program in superconductivity is gone. MPA's DOE Energy Efficiency and Renewable Energy programs have significant funding, but our prospects for new funding will have to wait until Congress passes a budget. MPA has made some progress in getting more weapons program funding. We would like to see this expand even more, as we believe we have a lot to contribute in fundamental materials understanding as well as novel diagnostics. We also have had some recent successes in global security, and people are promoting ideas for MPA contributions to defense technology. Both nuclear weapons and global security are major program areas for the Laboratory, and MPA could do well to participate more in these programs.

Given the current continuing resolution, and the budget uncertainty, the prudent thing for MPA as a Division is to be very conservative at this time. We need our employees to think carefully about expenditures. We will also benefit if MPA employees keep an eye out for opportunities to pursue new programs.

MPA Deputy Division Leader David Watkins

Wu… The Early Career Research Program is designed to strengthen the Laboratory's scientific workforce by providing support to exceptional researchers during their crucial early career years. The program provides funding up to $225,000 a year for up to two years.

"This is a very important experience for him," said Zelenay. "It's coming at the right time for his research career. He has done very well in the first six months of the project."

In his newest role, Wu can call upon his previous experience as a principal investigator. In 2004, as a postdoctoral fellow at Tsinghua University (Beijing, China) , he was awarded science funding and led a group that performed fundamental studies into electrolysis of water as a means of producing hydrogen for use as an energy source. In 2008 Wu joined the Laboratory as a postdoctoral researcher and a year ago became a technical staff member.

A member of the MPA-11 fuel cell team, Wu has more than 11 years of experience in materials electrochemistry and electrochemical characterization and analysis. During that time he's also shined as a team member.

Most recently, Wu and Zelenay developed a platinum-free catalyst in the cathode of a hydrogen fuel cell. As reported in *Science*, the catalysts—which Wu synthesized using carbon (partially derived from polyaniline in a high-temperature process), and inexpensive iron and cobalt instead of pricy platinum—yielded high power output, good efficiency, and promising longevity. The use of non-platinum group metal (non-PGM) catalysts could help reduce cost and accelerate commercialization of fuel cells.

Wu has also put his polyaniline-based catalyst synthesis expertise to work as a member of Zelenay's team that earned a 2010 Department of Energy Hydrogen Program R&D Award for its outstanding contributions to the advancement of fuel cell catalyst development, in particular its dramatic improvements in the performance of non-PGM catalysts.

"His synthesis skills are invaluable to us," Zelenay said. "He is the main expert in synthesis skills of new materials with specific properties."

In 2009, the polyaniline-derived cathode catalyst Wu developed at Los Alamos was selected by The United States Council for Automotive Research as a technical accomplishment, describing it as "the most convincing work to date showing the potential of non-PGM catalysts for fuel cell applications."

Wu became interested in alternative energy sources at Harbin, where in 2004 he earned his PhD in electrochemical engineering. After two years as a postdoctoral fellow at Beijing's Tsinghua University, he performed fuel cell catalyst and lithium ion battery studies for two years as a postdoctoral researcher at the University of South Carolina.

"I came to the U.S. because it may give me a chance to join the top research institutes and work with the most outstanding scientists to do the best research possible," Wu said.

That's the same reason he came to Los Alamos. "I really like all the facilities the Laboratory has to offer and the collaboration possibilities, as well as the positive teamwork atmosphere," he said.

Gang Wu's Favorite Experiment

What: Synthesis of the polyaniline-derived nonprecious metal catalyst

Where: MPA-11 materials synthesis laboratory, Los Alamos National Laboratory

When: 2008-2009

Why: By replacing the expensive platinum used as catalysts in fuel cells with non-precious metal versions capable of high activity and durability, these promising power sources could become a significant part of the world's energy portfolio. Currently, non-precious metal catalyst formulations suffer from poor stability in the acidic fuel cell environment. Enhanced performance durability of these catalysts remains strongly dependent on the materials synthesis methods and involved chemical reactions.

How: The researchers in situ polymerized aniline on the surface of carbon black nanoparticles and applied heat to obtain graphitized layered "hybrid" materials containing iron and cobalt units. An advantage of polyaniline is that it acts as the carbon and nitrogen sources simultaneously, potentially facilitating the formation of nitrogen-containing sites on the graphitic carbon surface during catalyst synthesis. Various transition metals such as iron and cobalt used in the synthesis ensue high performing oxygen reduction reaction activity and four-electron selectivity. Extensive electrochemical and physical techniques were used to explore the roles of each element and possible active sites.

The a-ha moment: By using a novel materials synthesis strategy, the researchers developed a stable non-precious metal catalyst in an acidic environment. This directly addressed the performance durability issue, which is the biggest barrier to using non-platinum materials in polymer electrolyte fuel cells.

Making metamaterials with sound waves in five minutes or less

In an important step in metamaterials development, Dipen Sinha (MPA-11) and collaborators have identified fast and inexpensive tools for engineering these materials.

Director's Postdoctoral fellow Farid Mitri (MPA-11), under the direction of Sinha and with material scientist Fernando Garzon (MPA-11), have described how to build artificial materials with unusual properties, such as negative refractive index that can lead to invisibility cloaking, in a mere five minutes or less. Until now, metamaterial synthesis was cost-prohibitive and required expensive equipment. The journal *Review of Scientific Instruments* published the research, and numerous scientific Web sites featured the work. Metamaterials are manmade structures exhibiting exotic properties. These materials can manipulate electromagnetic and acoustic waves to create invisibility cloaks, subwavelength focusing, and shielding. The combination of these intriguing properties poises metamaterials to make a significant impact on the technological world.

Sinha, Mitri, and Garzon have developed an easy and inexpensive method for fabricating a three-dimensional (3D) periodic structure using the radiation force induced by high-frequenc (greater than 1 MHz) acoustic waves in a resonator cavity. The process arranges nanoparticles in a host polymer matrix (e.g., epoxy). Changing the frequency of the acoustic waves can easily modify this arrangement. The scientists characterized its internal skeleton with x-ray micro-computed tomography (XμCT) to assess the quality of the manufacturing process. The particles can be made from any material and can be even hollow microspheres. This is important to create acoustic metamaterials where the particles behave as local mechanical resonators. The scientists used the state-of-the-art technique based on the radiation force of ultrasound standing (or stationary) waves in a rectangular chamber to pattern clusters of 5-nm-diameter diamond nanoparticles in parallel planes within a 3D matrix of epoxy before solidification. The periodic pattern became permanent with full cure of the epoxy matrix to form a 3D metamaterial structure. A wide variety of patterns and shapes can be created by applying the appropriate ultrasound field.

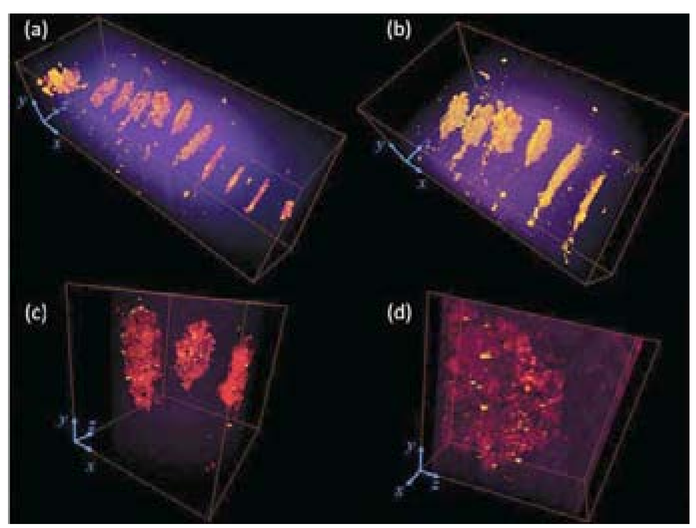
The ultrasound field was activated for 5 minutes, a duration corresponding to the epoxy curing cycle. During this time, clusters of diamond nanoparticles were trapped and patterned due to the acoustic radiation force that directs them toward the nodes of the standing wave field to form parallel periodic planes. The manufacturing time may be further reduced by selecting a faster curing epoxy (less than 1 minute). This is a bench-top and inexpensive fabrication approach.

This technique is particularly suited for creating materials with the length-scale (periodicity of the pattern) in the range of 1-100 micron where there is a gap in existing fabrication technology. For example, lithography techniques are available for small-scale fabrication (sub-micron length-scale), and mechanical machining techniques are used for materials created with mm-size objects.

An advantage of this fabrication technique is that the particles may consist of any material (metal, insulator, semiconductor, superconductor, piezoelectric, nanowires, or nanotubes, and even biological materials), and a wide range of geometries (cylindrical, hexagonal, and other symmetries) is possible. The researchers' goals are to develop novel sensors and devices based on this fabrication technique that extend beyond metamaterials.

Reference: "Characterization of Acoustically Engineered Polymer Nanocomposite Metamaterials using X-ray Microcomputed Tomography," *Review of Scientific Instruments* **82**, 034903 (2011). A Laboratory Director's fellowship provided financial support for the research. Cristian Pantea (MPA-11) provided the diamond-nanoparticle powder and experimental assistance, and Mark. A. Nelson (formerly MPA-11) assisted while using the x-ray computed tomography system. The work supports the Lab's Global Security and Energy Security mission areas and the Materials for the Future science pillar.

Technical contact: Dipen Sinha



XμCT renderings of a polymer nanocomposite metamaterial assembled using 1 MHz ultrasound standing wave field in which approximately 5-nm diameter diamond nanoparticles are clustered in a host fluid (epoxy) cured during 5 minutes to create the surrounding solid structure. (a) The 3D rendering using the 2°ø detector lens (resolution apprroximately 10 microns), in which all the patterned planes (i.e., 12 planes) of diamond-nanoparticle clusters are visible. [(b)–(d)] 3D rendered images at higher resolutions using the 4°ø, 10°ø, and 20°ø lenses, respectively.

Misra named ASM Fellow

Amit Misra (Center for Integrated Nanotechnologies, MPA-CINT) was recently named a Fellow of ASM International, selected by the organization's board of trustees in honor of his distinguished contributions in the field of materials science and engineering. Also selected were Robert Field (Materials Technology: Metallurgy, MST-6) and Deniece Korzekwa (Nuclear Materials Science, MST-16)

Misra was cited for "significant contributions to fundamental understanding of the mechanical behavior, radiation damage, and stability of metallic materials, particularly micro and nanolayered materials." Misra, the co-director of the Center for Materials at Irradiation and Mechanical Extremes (CMIME), an Energy Frontier Research Center sponsored by DOE Basic Energy Sciences, received his doctorate in materials science and engineering from the University of Michigan. He has worked at LANL for over 14 years. His research expertise is in defects and interfaces in materials, transmission electron microscopy, nanomechanics, and structural materials for nuclear energy.

Recipients of one of the highest honors in the field of materials, ASM Fellows are technical and professional leaders who have been recognized by their colleagues and now serve as advisors to the Society. The Fellows' guidance enhances the society's standing as a leading organization for materials with 36,000 members worldwide. The new Fellows will be honored during a ceremony in Columbus, Ohio.

MPA research selected as *PRB* editor's suggestion

Physical Review B, a journal of the American Physical Society, selected two papers by Tomasz Durakiewicz (Condensed Matter & Magnet Science, MPA-CMMS) and his collaborators for an editor's suggestion. "Editor's suggestions" are papers that the editors and referees of scientific journals find of particular interest, clarity, or importance.

The first paper, which Durakiewicz co-authored with scientists from Sweden (Uppsala University) and The Netherlands (Leiden University), is devoted to the electronic structure of URu_2Si_2, where the mysterious hidden-order phase is found below 17.5 K. By comparing a vast amount of published experimental results with their own calculations, the researchers showed that the itinerant treatment of uranium is needed to explain the electronic structure. The hidden-order transition itself is linked to the Fermi surface instability, characterized by partial gapping in specific parts of the Fermi surface. The researchers also discuss the differences between the hidden-order phase and large moment antiferromagnetic phase in URu_2Si_2, where they propose the same or very similar Fermi surfaces, but different order parameters are associated with both phases.

Their findings bring scientists closer to the full 3D mapping of the Fermi surface excitations in this most mysterious system, where the exact roles of spin and charge excitations in the formation of the hidden-order state are still poorly understood. In addition to being flagged as an "editor's suggestion," this paper was selected for *Synopsis in Physics*, where the results of interest to broad physics community are summarized by the *Physical Review* editors.

In the second paper, Durakiewicz teamed up with John J. Joyce (MPA-CMMS) as well as collaborators from Lawrence Berkeley National Laboratory; the University of California, Irvine; and Universite de Montreal in Canada, to explore the electronic structure of a heavy fermion system. They investigated the Yb occupancy in the $Ce_{1-x}Yb_xCoIn_5$ compound with a multitude of spectroscopic techniques: extended x-ray absorption fine structure, x-ray absorption near-edge structure, and angle-resolved photoemission spectroscopy. They learned that through the entire doping range both the f-hole occupancy for Yb and the f-electron occupancy for Ce are constant.

This "unexpected" and "novel" finding suggests that there is no mutual influence on orbital occupancy between Ce and Yb. Electronic structure was found to be insensitive to Yb occupation, which means the hybridization between Ce 4f electrons and conduction band electrons is not affected by Yb. The research team postulated the existence of two independent, but coexisting networks; one related to the Ce ions in the heavy-fermion limit, and one of Yb ions in intermediate-valent limit, with no charge transfer between Ce and Yb. This finding helps scientists understand the reasons behind relative insensitivity of superconductivity in Ce-substituted series when compared with In-site substitution.

Work on both projects was funded by the U.S. Department of Energy's Office of Basic Energy Sciences and Los Alamos's Laboratory Directed Research and Development program.

References: "Electronic structure theory of the hidden-order material URu_2Si_2," *Physical Review B* **82**, 205103 (2010); "Electronic structure and f-orbital occupancy in Yb-substituted $CeCoIn_5$," *Physical Review* B **83**, 235117 (2011).

Technical contact: T. Durakiewicz

HeadsUP!

Seasonal flu vaccine available through local pharmacies

Present your LANS Blue Cross Blue Shield card

The 2011 seasonal flu vaccine is available now from area pharmacies, clinics, and personal medical providers. LANS employees can receive the seasonal vaccine from many local providers and pharmacies without a co-pay by presenting their Blue Cross Blue Shield of New Mexico health plan card. Employees should call ahead to check hours and availability. Occupational Medicine will not be providing the flu vaccine onsite except for those LANL workers who receive the flu vaccine as part of their medical surveillance program.

In addition, the seasonal flu vaccine will be available free of charge at many community health fairs between now and the end of October. A list of locations in New Mexico contracted by Blue Cross Blue Shield of New Mexico to provide the seasonal flu vaccine at no out-of-pocket charge to individuals covered by the BCBS health plan is at http://int.lanl.gov/news/newsbulletin/pdf/vaccine_network_list_092810.pdf. Employees are encouraged to call pharmacies first to find out what times the flu vaccine will be offered.

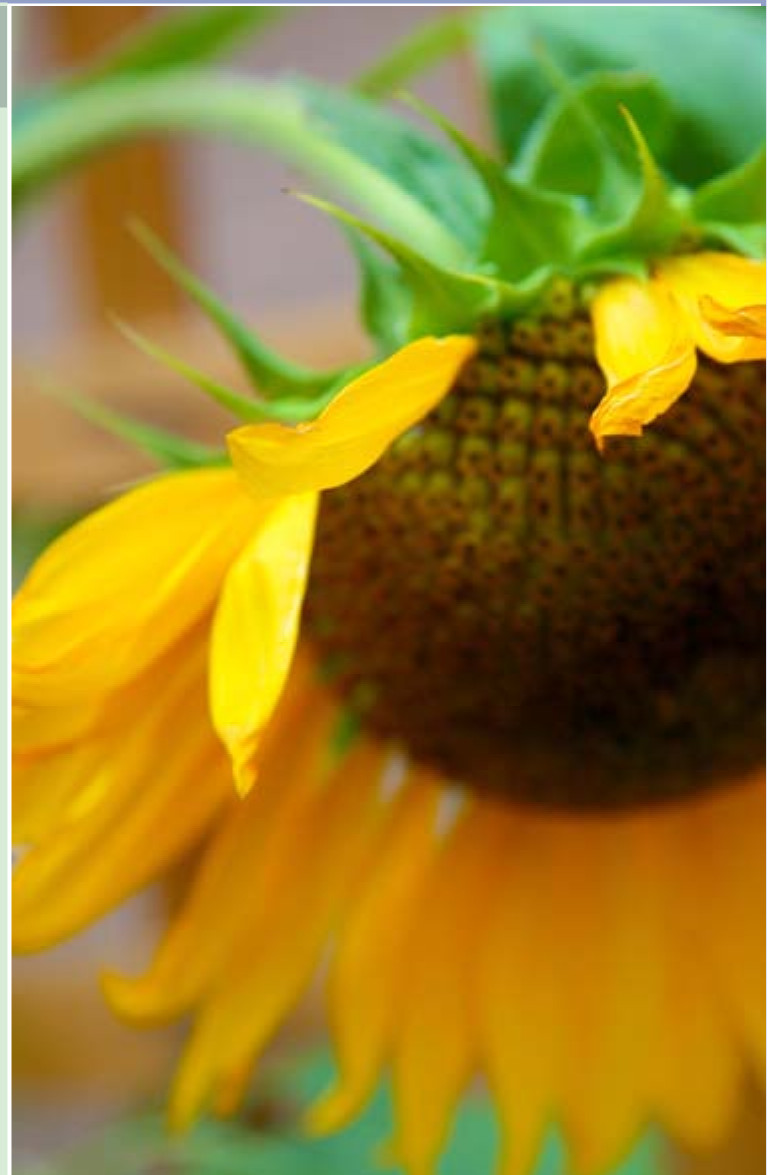
Tag your bags

Don't let your unattended belongings be mistaken for a suspicious package and "destroyed." Visit the Tag Your Bag webpage at int.lanl.gov/safety/emergency/emergency_management/tag_your_bag.shtml for more information on the importance of placing identification tags on bags and other personal carriers.

To report unattended and suspicious bags or packages, contact the Protective Force immediately at 7-4437.

Winter closure information

An all-employee memo about LANL's 2011 winter closure was issued by Associate Director for Business Services Mark Barth. Read the memo at int.lanl.gov/memos/2011/09/LANL-ALL2447.pdf for more information.



Celebrating service

Congratulations to the following MPA employees celebrating service anniversaries recently:

David Reagor, MPA-STC	25 years
Peter Goodwin, MPA-CINT	20 years
Brian Scott, MPA-MC	20 years
Jonathan Rau, MPA-MC	15 years
Stephen Ashworth, MPA-STC	10 years
Benjamin Davis, MPA-MC	5 years

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